Underwater Photocurable Adhesive Attachment System

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LONG-TERM GOALS

The long-term goal of the research is to expand mission capabilities of Naval Special Warfare (NSW) in the underwater attachment of munitions and sensor packages on a variety of surfaces, quickly, covertly, and under extreme environmental conditions.

OBJECTIVES

The objectives of this program are to adapt previously developed photo-curable adhesive technology into an underwater attachment system to support various loads and various environmental influences. Previous research has determined that photocurable adhesive technology will develop very high strengths, quickly, even under the most adverse environmental conditions. This effort is designed to adapt photocurable methacrylate and photocurable epoxy attachment systems based on a determined best illumination source and system. The primary thrust of this effort is to overcome conventional attaching technology limitations in providing NSW the capability to complete attaching tasks unrestricted of seawater conditions.

APPROACH

The goal of the program is to incorporate photocurable adhesive technology into an underwater bonding system to be used by NSW divers. In addition to the goal of minimizing time-on-target, the system must be adaptable to different bonding scenarios and mission packages. Adhesive technology to be utilized includes photocurable methacrylate systems developed and formulated by Virginia

Polytechnic Institute and State University and photocurable epoxies and acrylates developed by Rensselaer Polytechnic Institute. Both Virginia Tech and Rensselaer Polytech have contributed significantly to this effort in both identifying suitable technologies and the optimization of those technologies. The Coastal Systems Station (CSS) has been responsible for the convergence of the related technologies into a usable system for Navy divers.

WORK COMPLETED

The program has been focused in several different areas that include the formulation and development of adhesive systems, the development and optimization of optical/illumination system prototypes, the development of an adaptable system for attachments, and the identification of user-friendly system characteristics.

Both Virginia Tech and Rensselaer Polytech research groups have been attempting to develop and optimize photocurable adhesive systems to provide quick curing and robust bonding. Systems developed by Virginia Tech have been matched effectively to the source wavelength and appear to provide the quickest cure. Filler matching (settling) and robust adhesion are presently being addressed. The latest Rensselaer Polytech formulation appears to have the best overall adhesion, particularly to metals underwater. Presently, improvements in cure rate and shelf life stability are being addressed.

Optical and Lamp design efforts have been conducted both at the Coastal Systems Station and at Virginia Tech. Certain system parameters and characteristics have been identified which have led to the development of several prototypes. Presently, efforts are underway at the Coastal Systems Station to reduce the system profile and to increase the overall optical output.

Efforts have been conducted to develop an adaptable attachment system that will provide the ability to attach a variety of systems through a common interface or through a flexible system which is effective in reducing bond stresses. While the adaptable system was first conceptualized at the inception of the program, the addition of the flexible system is expected to increase the overall reliability and/or load carrying ability for certain types of attachments.

User inputs have been solicited and obtained in order to determine user-friendly characteristics for a photo-curable attachment system. Future design efforts and safety assessments will be conducted at the Coastal Systems Station to provide a user-friendly system to NSW.

RESULTS

Adhesive Development

Photocurable Adhesive development efforts have been undertaken at Rensselaer Polytechnic Institute and at Virginia Tech in an attempt to formulate acceptable adhesive systems that will provide quick and robust underwater attachment to a variety of materials. The best adhesive systems should provide the required attachment, while at the same time being safe and user-friendly, in addition to having a long shelf life under normal storage conditions.

To this end, Rensselaer Polytech and Virginia Tech have developed numerous formulations for evaluation and laboratory testing. Examples of formulations developed as part of this program are listed in Table 1.

Table 1. Examples of Photocurable Adhesive Formulations.
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Rensselaer Base Formulation		Virginia Tech Base Formulation	
VCHDO	34 % wt	Bis-GMA	32 % wt
DEVE3	34 %	DEGDA	16 %
PVAc	27 %	PMMA beads	50 %
IOC10	3.4 %	DMpT	1 %
Perylene	1 %	Camphorquinone	1 %

Dr. Crivello and his Rensselaer research team have investigated both epoxy and acrylate formulations. Adhesion has been found to be good in epoxy formulations where PVAc was added as an adhesion promoter. However, although PVAc is soluable in many acrylate monomers, the inclusion of PVAc in these systems was found to be poor to marginal. Other adhesion promoters evaluated include PBBA and PBMA. Future efforts by Rensselaer Polytech will include the investigation of new formulations that include the use of perylene as the photosensitizer, in addition to the screening of new long wavelength photosensitizers in hopes of finding a more acceptable alternative.

Dr. Love and the Virginia Tech research team have investigated several acrylate formulations, which have exhibited quick cure rates with the anticipated illumination source. The first formulation developed seemed very promising due to its quick cure rates and strong bonds. However, further testing underwater on metals revealed very poor adhesion due to the hydrophobic/hydrophillic mismatch between the adhesive and the underwater substrates. Replacement of the viscosity modifier with DEGDA appeared to improve adhesion on these materials underwater. However, a subsequent safety assessment conducted at the Coastal Systems Station prior to a field demo revealed that DEGDA is a severe poison, particularly through the skin. Due to the poisonous character of the formulation, special transportation and handling procedures are required, making the adhesive system undesirable for the intended application. Future efforts by Virginia Tech will be directed toward finding a safer substitute component for DEGDA that will not degrade performance. In addition, filler materials will be incorporated that do not settle over time.

Illumination Source Evolution

Previous efforts have focused on matching efficient illumination sources to adhesive systems under development. This has included the investigation of the incorporation of LED sources with peak outputs at 470nm and at 365nm. LED source designs have evolved from relatively low intensity systems to systems that will cure adhesives rapidly, particularly at 470nm. Unfortunately, cure at 365nm has not been as productive both because of the low output of this type of UV LED and also due to the characteristics of available adhesive system components.

Source design and improvements have been made both at the Coastal Systems Station and at Virginia Tech. The Virginia Tech early design illumination output was approximately 3.5mw/cm2. Subsequent research at CSS demonstrated that for short term operation, the LEDs can be overdriven beyond the

rated specifications to produce a more intense output and quicker cure. Subsequent designs at CSS and at VPI have resulted in improved performance. Figures 1 through 3 illustrate lamp evolution to date. Future efforts will be directed toward increasing the output further, in addition to miniaturization of the entire system to an appropriate size for use and transport.

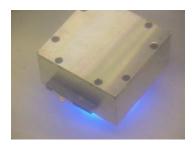


Figure 1. Early VPI lamp design, with output ~ 3.5 mw/cm2.



Figure 2. Early CSS lamp design with hard-eye insert. The recessed cutaway was necessary for the hard-eye mount design. Improvements in padeye design at CSS eliminated this necessity, and made it possible for a solid LED array, and a simplified operation



Figure 3. CSS LED array incorporated into a miniaturized system.
Future efforts will be directed toward incorporation of highoutput LED systems into this and other more userfriendly configurations.

Attachment System

Since the inception of the program, the goal has been to produce an adaptable attachment system that will accommodate various attachments through a common interface. For certain types of attachments, improvements have been made in the load carrying ability over conventional systems through the use of a flexible loop instead of a rigid eye. These improvements have resulted in both the ease of lamp manufacturing and also in the ease of operation. Figures 4 and 5 show the early and improved systems. In addition to the flexible loop, a twist-lock edge mount first conceptualized at CSS was included in Virginia Tech prototypes for testing.

Packaging

Numerous packaging options of photocurable adhesives have been identified, including commercial products, in addition to custom alternatives that may be more suitable for the application.

IMPACT/APPLICATIONS

Overcoming conventional environmental constraints of underwater bonding will expand forward military opportunities in addition to providing direction for future systems development that require bonding, both topside and underwater.



Figure 5. Flexible loop system developed at CSS removes stresses due to moment and torsion. One step operation.



Figure 4. VPI wingnut design based on MK84 padeye. This design requires a two step operation when used with lamp in Figure 1. The disk is bonded and then the padeye is screwed_onto the disk.

TRANSITIONS

This program is being jointly funded by United States Special Operations Command (USSOCOM). The technology is applicable to many Special Operations Forces (SOF) and Explosives Ordnance Disposal (EOD) mission scenarios. The most likely transition paths are through the Very Shallow Water Mine Countermeasures (VSW MCM) Detachment or through a USSOCOM program. Other fleet and commercial uses are expected in applications that require quick bonding and attachment, particularly under cold and/or wet conditions.

RELATED PROJECTS

A 6.2 Underwater Surface Preparation Technology Development Program. This program is investigating and developing new technologies for preparing marine surfaces for adhesive bonding.

REFERENCES

- S.E. Gorin, Underwater Adhesives and Non-Metallic Attaching Techniques Requirements, CSS/TN-96/7, Naval Surface Warfare Center, Dahlgren Division.
- J. Crivello, 1998. Photo- and Redox Curable Epoxy Adhesives for Underwater Applications, Rensselaer Polytechnic Institute.
- B. Love, W. Grant, and C. Holton, 1998. Energy Assisted Adhesive Characterization for Marine Applications: Stage II Light Curing Adhesive Feasibility Study, Virginia Tech..

PUBLICATIONS

Dolez, P.I., R. Anderson, M. Marek and B.J. Love, Photocuring Induced Adhesion Evolution in Marine Systems, submitted to *Journal of Polymer Science and Technology*.

Dolez, P., M. Marek and B.J. Love, Photopolymerizable Acrylic Resin: Effect of the Curing Time and Temperature, submitted to the *Journal of Applied Polymer Science*.

Jensen, M.K, B.J. Love, J.W. Grant, J. Cotton, J.R. Keiser, and D.F. Wilson, 2000. Comparison Study of Dicyandiamide-cured Epoxy Bonded Steel Joints and Polyamidoamine-cured Epoxy Bonded Steel Joints, *International Journal of Adhesion and Adhesives*, 20, 437-444.

Cotton, J., J.W. Grant, M.K. Jensen and B.J. Love, 2000. Analytical Solutions to the Shear Strength of Interfaces Failing Under Flexure Loading Conditions, *International Journal of Adhesion and Adhesives*, in press.

PATENT APPLICATIONS

Courson, Billy, Jody Wood and Brian Love, Chemiluminescent Photo-Curable Adhesive Curing and Bonding System, Navy Case No. 79295.

Love, Brian, Tom Kuhr, Carvel Holton, J. Wallace Grant, Billy Courson and Richard Claus, Light Cured Adhesive for Marine and Civil Infrastructure Applications, VTIP# 98.008.

Courson Billy, and Ray Baggett, Universal and Adaptable Padeye System, Navy Case No. 82523. Holton, Carvel, Brian Love and P.I. Dolez, Hydrophilic photocurable adhesive for marine applications, VTIP # 00-121.